Technical Paper 65

DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
JOSEPH A. HOLMES, DIRECTOR

UNIVERSITY LIBRARY
DEC 9 1914
PRINCETON, N. J.

A STUDY OF THE OXIDATION OF COAL

BY

HORACE C. PORTER AND O. C. RALSTON

WASHINGTON
GOVERNMENT PRINTING OFFICE
1914

The Bureau of Mines, in carrying out one of the provisions of its organic act—to disseminate information concerning investigations made—prints a limited free edition of each of its publications.

When this edition is exhausted copies may be obtained at cost price only through the Superintendent of Documents, Government Printing Office, Washington, D. C., who is the authorized agent of the Federal Government for the sale of all publications.

The Superintendent of Documents *is not an official of the Bureau of Mines*. His is an entirely separate office and he should be addressed:

SUPERINTENDENT OF DOCUMENTS,
Government Printing Office,
Washington, D. C.

The general law under which publications are distributed prohibits the giving of more than one copy of a publication to one person. Additional copies must be purchased from the Superintendent of Documents. The price of this technical paper is 5 cents.

First edition. August, 1914.

CONTENTS.

	Page.
Introduction	5
Oxidation of coal at ordinary temperatures	5
Spontaneous heating of coal	5
Factors affecting the ignition of coal and other substances	6
The initial action of oxygen on coal	6
Experiment to show exothermic character of action	8
Method employed and results obtained	8
Comparison of rate of oxidation of different coals	9
Description of apparatus and method of using	10
Descriptions and analyses of coals tested	12
Results of experiments	12
Discussion of results	13
Factors affecting rate of oxidation of coal	13
Variation of temperature	13
Variation of oxygen pressure	14
Reduction of proportion of oxygen below that in normal air	14
Addition of carbon dioxide to atmosphere	15
Discussion of results of tests	15
Experiments to determine nature of oxidation reactions	17
Description of apparatus and of methods used	17
Results of tests	19
Conclusions from results of tests	20
Relative quantities of products of oxidation	23
Nature of the oxidizing action	24
Inflammability of coal dust	26
Other conclusions from results of tests	27
Publications on fuel technology	29

ILLUSTRATIONS.

Page.

FIGURE 1. Behavior of coals in current of 50 per cent oxygen at 140° and 160° C. 7

2. Apparatus for comparing rate of oxidation of coals 11

3. Comparison of rate of oxidation of four coals 13

4. Rate of oxidation of coal No. 48 (Illinois) at different temperatures .. 15

5. Rate of oxidation of coal No. 48 (Illinois) under varying pressures of oxygen 16

6. Rate of oxidation of coal No. 48 (Illinois), as affected by percentages of oxygen in air 16

7. Apparatus for measuring products of oxidation 18

8. Amounts of water, CO_2, and CO produced in the oxidation of coal No. 43 (Wyoming) 21

9. Amounts of water, CO_2, and CO produced in the oxidation of coal No. 48 (Illinois) 22

10. Amounts of water, CO_2, and CO produced in the oxidation of coal No. 650 (Pittsburgh) 23

11. Composition of oxidation products from coals No. 43 (Wyoming), No. 48 (Illinois), and No. 650 (Pittsburgh) 24

12. Increase of weight in coals No. 43 (Wyoming), No. 48 (Illinois), and No. 650 (Pittsburgh), by oxygen fixation 25

TABLES.

Page.

TABLE 1. Heat developed by fixation of oxygen in 80-gram dry sample, coal No. 43 (Wyoming) 9

2. Description and analyses of coals 12

3. Comparison of rate of oxidation of four coals 12

4. Rates of oxidation of coal at different temperatures 13

5. Rates of oxidation of coal at different oxygen pressures 14

6. Rates of oxidation of coal in normal air and in air with reduced oxygen percentages 14

7. Rates of oxidation of coal in air as affected by different percentages of carbon dioxide (oxygen remaining constant) 15

8. Water produced by oxidation of three coals—No. 43 (Wyoming), No. 48 (Illinois), and No. 650 (Pittsburgh)—at different temperatures .. 19

9. CO_2 produced by oxidation of three coals—No. 43 (Wyoming), No. 48 (Illinois), and No. 650 (Pittsburgh)—at different temperatures 19

10. CO produced by oxidation of three coals—No. 43 (Wyoming), No. 48 (Illinois), and No. 650 (Pittsburgh)—at different temperatures 20

11. Change in weight of three coals—No. 43 (Wyoming), No. 48 (Illinois), and No. 650 (Pittsburgh)—caused by oxidation at different temperatures 20

A STUDY OF THE OXIDATION OF COAL.

By Horace C. Porter and O. C. Ralston.

INTRODUCTION.

Combustion, in the broad sense of the word, is oxidation accompanied by the production of heat, and includes those slow oxidation processes in which heat is produced at a rate so slow that it often does not manifest itself by a rise in temperature. The rate of oxidation of combustible material during the period preceding ignition is, no doubt, one of the factors determining ease of ignition, and, in view of the varied and important manifestations of this property in connection with the mining and utilization of fuel, the subject has been given special study by the Bureau of Mines in its investigations relating to fuels belonging to or for the use of the United States.

OXIDATION OF COAL AT ORDINARY TEMPERATURES.

The fact is well known that the oxidation of coal is not restricted to those ranges of temperature in which active burning with incandescence and flame occurs. At ordinary temperatures coal exposed to the air undergoes oxidation. Weathering of coal, and the consequent deterioration in fuel value, result not from loss of volatile combustible gases, but almost exclusively from combination of the coal with oxygen, which takes place in such manner that much of the oxygen is retained by the coal and a part of the combustible constituents becomes neutralized or inert.

A good coking coal loses much of its coking quality by preliminary heating in air for a short period at 200° to 300° C., or by long exposure to the weather. Anderson[a] has shown that this change in the coal is due to oxidation.

SPONTANEOUS HEATING OF COAL.

Spontaneous heating of coal results, not from a self-contained, fermentationlike process within the coal, but from the slow oxidation of the coal substance or its mineral impurities by the oxygen of the air. Spontaneous heating can not occur when air is excluded.

---

[a] Anderson, W. C., Phil. Soc. Glasgow, vol. 29, 1897–98, pp. 72–96.

That some coals become heated by oxidation much more easily than others is shown by figure 1, which presents the results of heating six different coals, and a sample of a "sulphur parting" at constant temperatures in a current of oxygen.

FACTORS AFFECTING THE IGNITION OF COAL AND OTHER SUBSTANCES.

Other conditions being equal, the ease with which fine coal dust suspended as a cloud in air ignites is dependent on the relative rate of reaction of the coal substance with oxygen. Ease of ignition is, in general, largely determined by ease of oxidation. Any combustible substance that enters easily into reaction with oxygen while it is being heated will ignite easily. There are variations in the degrees of inflammability of different coal dusts when subjected to the conditions of dust explosions in mines, and also in the ease of ignition, or so-called "ignition points," of various solid substances when burned in other ways.

Combustible materials when thin, as paper or wood shavings, ignite easily because of the relatively large surface that they present for oxidation and because of the rapidity with which the material oxidizes. If a flame be applied for ignition another important factor comes into play; that is, the ease with which the material distills inflammable gases. This factor, however, appears to be not the principal one, since many finely divided solids ignite at temperatures below the ignition points of any gases distilled from them, so far as the ignition points of these gases are known. Compact masses of solids do not ignite easily, since they expose relatively small surface to oxidation.

THE INITIAL ACTION OF OXYGEN ON COAL.

At ordinary temperatures coal absorbs oxygen from the air through an addition reaction and thereby increases in weight, as shown by the early work of Richters,[a] corroborated by several later investigators.[b] The nature of this reaction has not been demonstrated, although Boudouard suggested that certain substances in the coal

---

[a] Richters, E., Ueber eine eigenthümliche Veränderung, welche die Steinkohle beim Erhitzen erleidet: Dinglers' Polytech. Jour., vol. 190, 1868, pp. 398–401; Beiträge zur Kenntniss des Verhaltens der Kohle zum Sauerstoff, vol. 193, 1869, pp. 51–61; Über die Veränderungen welche die Steinkohle beim Lagern an der Luft erleiden, vol. 195, 1870, pp. 315–331, 449–458.

[b] Fayol, H., Études sur l'altération et la combustion spontanée de la houille exposée a l' air: Bull. Soc. ind min., vol. 8, ser. 2, 1879, p. 487.

Dennstedt, M., and Hassler, F., Die Gefahren der Steinkohle, die Explosiongefahr: Zeit. angew. Chem., vol. 21, pt. 1, 1908, p. 1060.

Dennstedt, M., and Bünz, R., Die Gefahren der Steinkohle, die Selbstenzündlichkeit: Zeit. angew. Chem., vol. 21, pt. 2, 1908, p. 1825.

Boudouard, O., Études sur les charbons, produits résultants de leur oxydation: Bull. Soc. chim. France, ser. 4, vol. 5, 1909, pp. 377, 380.

Taffanel, J., De l'alteration des poussières de houille exposées a l'air: Original Communications, Eighth Intern. Cong. App. Chem., vol. 10, 1912, p. 277.

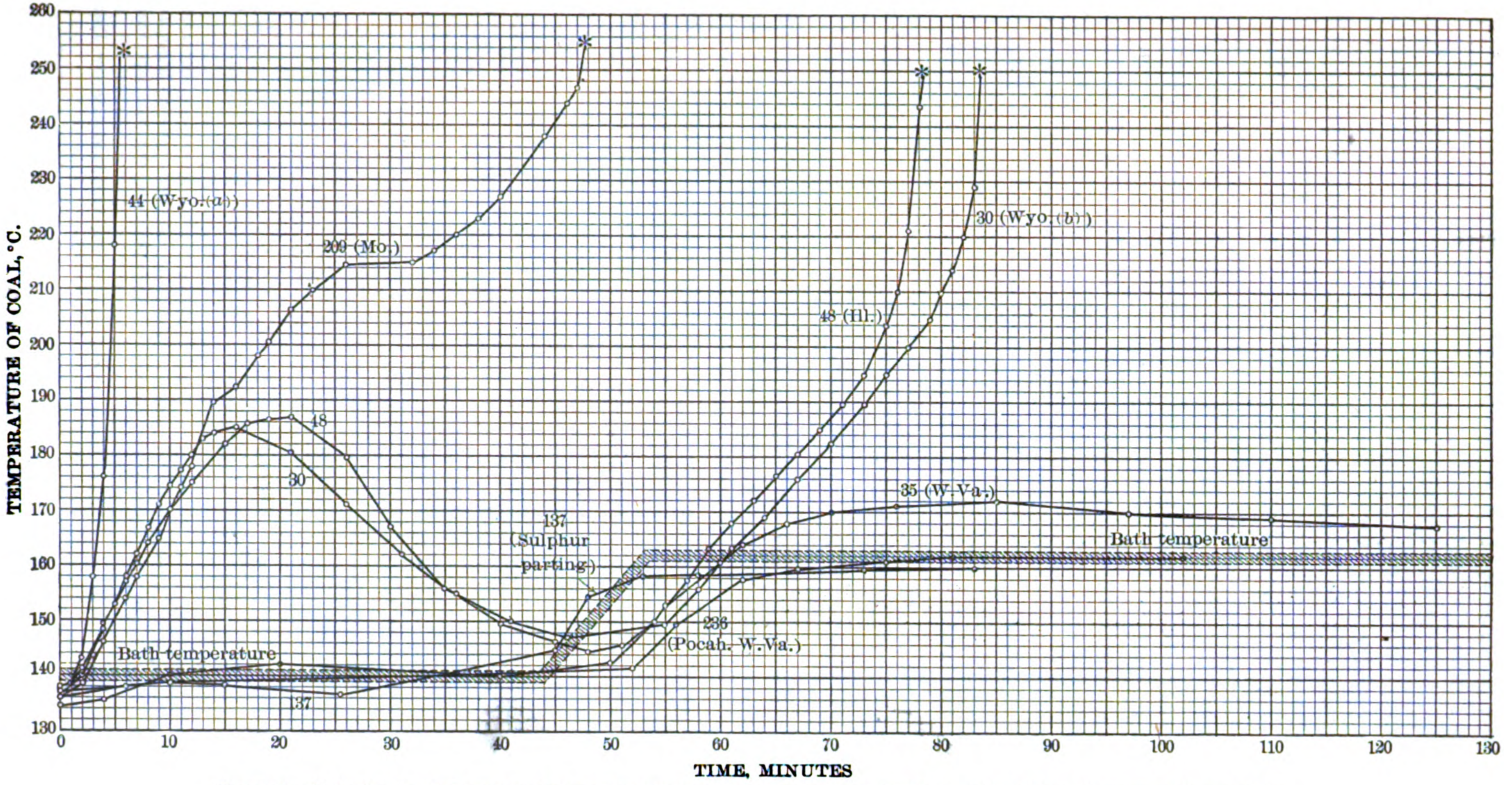

FIGURE 1.—Behavior of coals in current of 50 per cent oxygen at 140° and 160° C. *=Ignition. Rate of flow of oxygen, 4 liters per hour.

united with oxygen in such a manner as to produce humic acid or derivatives closely related to it.

Investigations of the Bureau of Mines on the escape of gas from broken coal[a] at ordinary temperatures have shown that although oxygen is rapidly absorbed by the coal, the amount of carbon dioxide produced thereby is relatively very small. During five months' exposure to air in a bottle, in which pure oxygen was admitted as rapidly as it was absorbed, a coarsely crushed sample of Illinois coal, from Franklin County, absorbed 5.3 liters of oxygen per kilogram (0.085 cubic foot per pound) and produced only 0.042 liter of carbon dioxide per kilogram (0.0007 cubic foot per pound), less than one one-hundredth of a molecularly equivalent amount of carbon dioxide compared to the oxygen. The possibility of oxidation of the hydrogen of coal and separation of the water thus formed was not investigated at that time, and the reaction appeared to be almost entirely a fixation of oxygen by the coal substance. Hillebrand[b] suggests the possibility of the loss of hydrogen from coal by oxidation to form water during preliminary air drying and also during final drying in air at 105° C. Some experimental data bearing upon this question are given on pages 17–20.

EXPERIMENT TO SHOW EXOTHERMIC CHARACTER OF ACTION.

Whatever may be the nature of the initial action of oxygen on coal. there is no question of its exothermic character. Taffanel[c] considers that the diminution of calorific value of the coal by fixation of oxygen is ample proof of this fact. An experiment performed in the laboratory of the bureau with coal No. 43 (subbituminous coal from Sheridan, Wyo.), exposed to pure oxygen at 41°–42° C. also proves this point.

METHOD EMPLOYED AND RESULTS OBTAINED.

After drying over calcium chloride at 100° C. in a partial vacuum of 25 mm., 80 grams of 60-mesh powdered coal was placed in a Dewar tube surrounded by a water bath at 41° to 42° C. The tube was exhausted to about 25 mm. and temperatures in the coal and in the surrounding bath were read by means of calibrated thermometers. When the coal temperature became constant within 0.5° of that of the bath, carefully dried oxygen was admitted until the pressure was slightly greater than 1 atmosphere. The temperature of the coal rose immediately above that of the bath, and within two hours had risen 11°, having also by transmission of its own heat raised the temperature of the surrounding bath more than 5°. The results are given in the following table:

---

[a] Porter, H. C., and Ovitz, F. K., The escape of gas from coal: Tech. Paper 2, Bureau of Mines, 1911. See also, Chamberlin, R. T., Notes on explosive mine gases and dusts, Bull. 26, Bureau of Mines, 1911.

[b] Hillebrand, W. F., Errors in the determination of moisture in coal: Original Communications, Eighth Intern. Cong. App. Chem., 1912, vol. 10, p. 188.

[c] Taffanel, De l'alteration des poussières de houille exposées a l'air: Original Communications, Eighth Intern. Cong. App. Chem., 1912, vol. 10, p. 283.

Table 1.—*Heat developed by fixation of oxygen in 80-gram dry sample, coal No. 43 (Wyoming).*

Time.	Temperature of bath.	Temperature of coal.
Hr. min.	*° C.*	*° C.*
20	41.5	42
24	(a)	....
25	41.5	42.5
30	41.5	43.4
35	42.0	44.2
43	42.0	45.6
50	42.0	46.9
1	43.0	47.0
1 15	44.5	49.7
1 25	44.0	50.8
1 44	45.0	52.2
2	46.5	52.8
19	54.5	56.2

[a] Oxygen admitted.

DISCUSSION OF RESULTS.

No effort was made to measure quantitatively the heat produced in this experiment, but the result shows qualitatively beyond any question that the action of oxygen on the coal at 42° C. developed a considerable amount of heat. The action at this temperature and under these conditions is in part a fixation of oxygen by the coal, and only in slight degree an attack on carbon to form carbon dioxide. As shown later in this paper, the hydrogen of the coal is probably attacked also in the early stages of oxidation. This heat from the action of oxygen at ordinary temperature is the primary cause of spontaneous combustion.[a]

COMPARISON OF RATE OF OXIDATION OF DIFFERENT COALS.

Figure 1 (p. 7) shows the difference between coals in their rates of heat development by oxidation, these differences being caused by the differences in rates of oxidation.

In order to determine more exactly the comparative rates of reaction of oxygen with different coals at temperatures below 200° C., an apparatus was devised on the static principle. A weighed sample of dry coal was allowed to stand in a closed apparatus in contact with pure dry oxygen at a pressure reduced so as to equal the average partial pressure of the oxygen in air. As oxygen was removed by fixation in or reaction with the coal, the supply was continually replenished from a measuring burette so as to maintain a constant pressure of gas in the apparatus.

---

[a] Recent investigations in England have determined calorimetrically the heat of oxygen absorption by coal. See Lamplough, F. E. E., and Hill, A. M. The slow combustion of coal dust and its thermal value: Trans. Inst. Min. Eng., vol. 45, 1913, p. 629.

The formation of other gases, either by the decomposition or the oxidation of coal, introduces an error into this method unless these gases are continually removed by absorbents or other means, as they exert a certain partial pressure and reduce by that much the partial pressure of oxygen required to keep the total gas pressure constant. Accordingly, a vessel containing phosphorous pentoxide was placed in the apparatus next to the sample of coal, in order to remove the water vapor formed by oxidation, and a vessel of soda lime to absorb carbon dioxide. It was found, however, that the rate of diffusion of carbon dioxide in the gaseous mixture and its absorption by dry soda lime was slow, and, therefore, tests above 140°, where the formation of carbon dioxide becomes more rapid, involved a considerable error. More or less carbon monoxide also was formed, which introduced an additional error.

DESCRIPTION OF APPARATUS AND METHOD OF USING.

The apparatus (fig. 2) consisted of a horizontal glass tube 30 cm. long whose inside diameter was 15 mm., closed at one end and surrounded for 20 cm. of its length by an electric heater. The open end of this tube was joined by means of marine glue to the cup-shaped end of another glass tube of 2 mm. bore, to which were sealed in turn at successive right-angled branches, a delicate manometer, a burette containing the supply of oxygen, a reservoir containing oxygen at a definite reduced pressure, and a Töpler mercurial vacuum pump, glass stopcocks being placed as required. A gram of coal was spread about 1 mm. thick on a boat 15 cm. long, of 200-mesh brass wire screen so fashioned that the oxygen could find contact from above and below.

The coal, freshly pulverized to the desired size (usually between 80 and 100 mesh) was weighed quickly, placed in the apparatus and thoroughly dried with phosphorus pentoxide for at least two hours at 110° C., or at the temperature of the oxidation experiment to follow, and in a vacuum of less than 2 mm. The temperature was then brought to the desired degree and oxygen was admitted from the reservoir, where it had been stored previous to the experiment at approximately the reduced pressure desired. The manometer was read quickly and additional oxygen was then admitted at regular intervals from the burette at such a rate that the gas pressure was maintained constant.

In order to attain greater delicacy in the manometer readings than was possible with a mercury column, and at the same time use a wide range of pressures in different experiments, an auxiliary manometric device was attached to the mercury manometer as shown at *m*, figure 2. On one arm of the manometer, between the mercury

Digitized by Google Original from PRINCETON UNIVERSITY

column and the apparatus, was attached an auxiliary gage *m′*, shaped like a U, with the upper ends turned inward and joined together through a T-bore cock *k*, to which was connected the side tube leading from the manometer. By means of the cock the auxiliary tube could be opened from one or both of its arms to the manometer. One arm of the auxiliary tube was connected to a closed bulb of about 50 c. c. capacity, surrounded by a water jacket. Olive oil was used in the auxiliary gage on account of its negligible vapor pressure. The initial pressure reading was taken on the mercury manometer, both arms of the auxiliary gage being open so that the level of liquid in them was the same. The cock was then turned so as to communicate with only one arm, and to close the arm to which the bulb was attached. The mercury column was thus replaced by the more delicate oil column for use during the experiment in maintaining constant pressure.

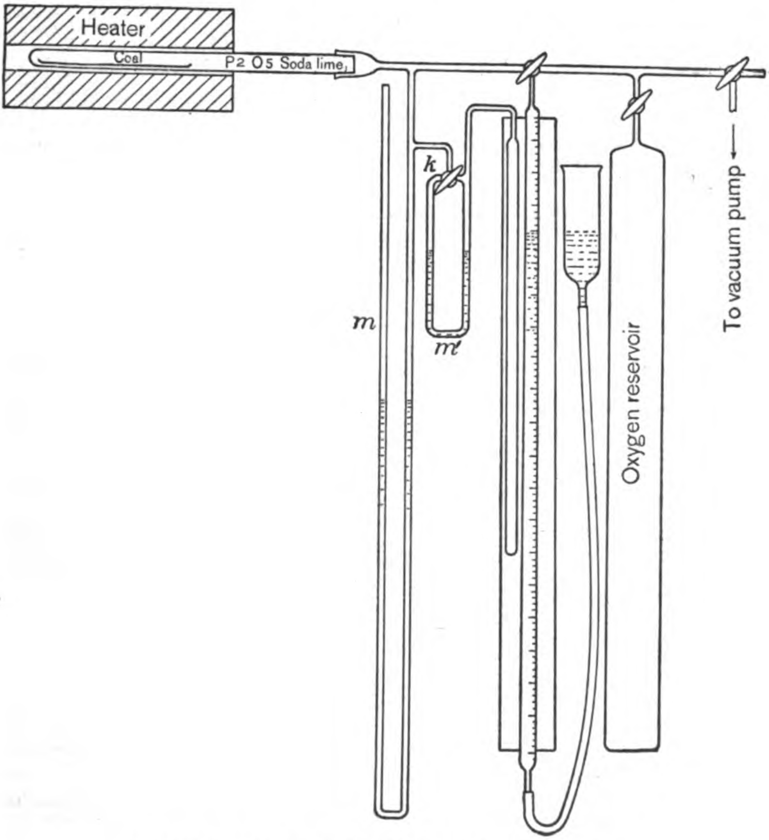

FIGURE 2.—Apparatus for comparing rate of oxidation of coals.

DESCRIPTIONS AND ANALYSES OF COALS TESTED.

The samples of coal whose oxidation rate was compared are described in the following table. They were chosen as being representative of four widely different types:

TABLE 2.—*Description and analyses of coals.*

Laboratory No.	Source of sample.	Kind of coal.	Moisture.	Volatile matter.	Fixed carbon.	Ash.	Sulphur.	Calorific value.
			P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*Cal.*
43 (Wyo.)..	Dietz, Sheridan Co., Wyo. (Mine sample.)	Subbituminous.	21.02	33.50	40.08	5.40	0.81	5,353
48 (Ill).....	West Frankfort, Franklin Co., Ill. (Mine sample.)	Bituminous...	7.54	32.00	52.98	7.48	.99	6,850
395 (Pittsburgh.)	Baird, Washington Co., Pa. (Car sample.)	.....do........	1.81	34.20	57.49	6.50	.92	7,786
9614 (W. Va.)	Sun mine, New River district Fayette Co., W. Va. (Mine sample.)	Semibituminous.	1.13	20.50	72.88	5.49	2.03	8,123

RESULTS OF EXPERIMENTS.

The results in the following tables have been computed to the basis of dry coal and are expressed as cubic centimeters of oxygen (at 25° C. and 760 mm. pressure) consumed in the reaction with 1 gram of dry coal, 80 to 100 mesh fine.

For comparison of different coals, the tests were run at 140° C. on coal sized between 80 and 100 mesh, and at a pressure of oxygen as nearly as practicable 150 mm. The results of tests with four different coals are given in Table 3.

TABLE 3.—*Comparison of rate of oxidation of four coals.*

[Temperature 140° C.; fineness 80 to 100 mesh.]

Laboratory No. of sample.	Date of test.	Oxygen pressure.	Amount of oxygen consumed per gram of dry coal in—						
			5 minutes.	10 minutes.	20 minutes.	40 minutes.	60 minutes.	90 minutes.	120 minutes.
	1912.	*Mm.*	*C. c.*	*C. c.*	*C. c.*	*C. c.*	*C. c.*	*C. c.*	*C. c.*
43 (Wyo.)................	Aug. 21	153	7.1	9.9	14.1	20.6	26.1	....	....
48 (Ill.)................	Sept. 24	149	1.3	2.3	4.0	6.6	8.7	....	....
Do.................	Oct. 18	156	1.7	3.0	5.1	8.2	11.0	....	....
Do.................	Dec. 11	149	1.7	2.9	4.9	8.2	10.7	....	....
395 (Pittsburgh).........	Aug. 23	160	0.7	1.2	2.0	3.3	4.5	6.1	7.5
Do.................	Aug. 27	143	0.6	1.1	1.7	2.9	3.9	....	....
Do.................	Aug. 28	152	0.6	1.0	1.7	2.9	4.0	5.5	6.8
9614 (W. Va.)............	Aug. 13	144	0.3	0.5	1.1	1.7	2.4	3.3	....

DISCUSSION OF RESULTS.

From Table 3 and figure 3 may be seen the wide variation between coals in their rates of oxidation. This variation conforms closely to the known variation between these kinds of coal in inflammability and ease of ignition, as well as in their tendencies to deteriorate or to become heated spontaneously when exposed to the air.

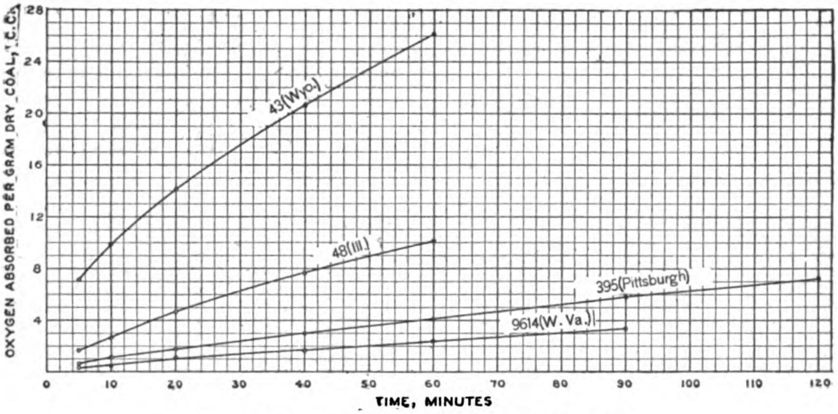

FIGURE 3.—Comparison of rate of oxidation of four coals.

FACTORS AFFECTING RATE OF OXIDATION OF COAL.

VARIATION OF TEMPERATURE.

A series of tests to determine the effects of variation of temperature on the rate of oxidation was made with coal No. 48 (Illinois). The temperatures at which the tests were made ranged from 40° to 240° C. The results are given in Table 4, as follows:

TABLE 4.—*Rates of oxidation of coal at different temperatures.*

[Coal No. 48 (Illinois). Fineness 80 to 100 mesh.]

Date of test.	Temperature.	Oxygen pressure.	Amount of oxygen consumed per gram of dry coal in—				
			5 minutes.	10 minutes.	20 minutes.	40 minutes.	60 minutes.
1912.	° C.	*Mm.*	*C. c.*	*C. c.*	*C. c.*	*C. c.*	*C. c.*
Oct. 3	40	161	0.06	0.09	0.13	0.17	0.21
Oct. 2	70	150	.09	.12	.15	.24	.30
Sept. 30	100	167	.61	.91	1.35	2.12	2.82
Dec. 14	100	149	.55	.78	1.24	1.98	2.60
Oct. 4	120	150	.92	1.45	2.38	3.91	5.20
Dec. 13	120	151	1.01	1.64	2.68	4.74	5.78
Sept. 24	140	149	1.35	2.30	3.96	6.56	8.71
Oct. 18	140	156	1.70	3.00	5.08	8.21	11.04
Dec. 11	140	149	1.73	2.89	4.93	8.22	10.74
Oct. 5	170	150	2.83	5.03	8.87	14.68	19.34
Oct. 7	200	150	4.61	7.74	13.58	21.63	27.68
1913.							
Mar. 13	200	150	4.33	8.35	14.47	24.44	32.44
Mar. 14	240	150	4.22	9.19	14.62	21.09	24.87

VARIATION OF OXYGEN PRESSURE.

Tests were also made to determine the effect of varying the pressure of the oxygen. Samples of coal No. 48 (Illinois) were used in these tests. The pressures ranged from 47 to 557 mm., the temperature being kept at about 140° C. in all tests. The results are given in Table 5.

TABLE 5.—*Rates of oxidation of coal at different oxygen pressures.*

(Coal No. 48 (Illinois), temperature 140° C. Fineness 80 to 100 mesh.)

Date of test.	Oxygen pressure.	Amount of oxygen consumed per gram of dry coal in—				
		5 minutes.	10 minutes.	20 minutes.	40 minutes.	60 minutes.
	Mm.	*C. c.*	*C. c.*	*C. c.*	*C. c.*	*C. c.*
Sept. 25, 1912	47	0.76	1.35	2.30	3.94	5.26
Sept. 20, 1912	84	.87	1.58	2.81	4.80	6.49
Dec. 16, 1912	100	1.53	2.34	3.85	6.33	8.27
Dec. 17, 1912	100	1.44	2.42	4.03	6.52	8.60
Dec. 18, 1912	110	1.45	2.46	4.25	7.19	9.61
Dec. 19, 1912	120	1.58	2.67	4.40	7.25	9.59
Jan. 30, 1913	130	1.39	2.40	4.11	7.15	9.68
Jan. 3, 1913	142	1.57	2.76	4.76	7.82	10.43
Dec. 11, 1912	149	1.73	2.89	4.93	8.22	10.74
Oct. 18, 1912	156	1.70	3.00	5.08	8.21	11.04
Sept. 26, 1912	266	1.91	3.06	5.26	8.49	10.95
Mar. 19, 1913	270	2.11	3.46	5.65	9.19	12.22
Mar. 20, 1913	400	2.52	4.13	7.35	11.44	14.81
Sept. 5, 1912	557	3.69	5.96	9.31	14.67	19.25

REDUCTION OF PROPORTION OF OXYGEN BELOW THAT IN NORMAL AIR.

Tests to determine the rates of oxidation in an atmosphere containing less oxygen than that normally present in air, as compared with the rate of oxidation in normal air, were made with samples of coal No. 48 (Illinois). The proportion of oxygen in the atmosphere used in the tests ranged from 20.9 to 9 per cent. The temperature was kept at about 200° C. in this series of tests. The results are given in Table 6.

TABLE 6.—*Rates of oxidation of coal in normal air and in air with reduced oxygen percentages.*

[Coal No. 48 (Illinois). Temperature 200° C., fineness 80 to 100 mesh.]

Date of test.	Oxygen[a] in atmosphere.	Barometer reading.	Amount of oxygen consumed per gram of dry coal in—				
			5 minutes.	10 minutes.	20 minutes.	40 minutes.	60 minutes.
1 13.	*Per cent.*	*Mm.*	*C. c.*	*C. c.*	*C. c.*	*C. c.*	*C. c.*
Jan. 21	20.9	742	1.82	3.10	5.03	8.01	10.28
Feb. 6	20.9	747	2.26	4.09	6.79	10.02	12.60
Mar. 3	20.9	748	1.82	3.00	4.91	7.15	10.88
Feb. 3	18.0	740	2.31	4.00	6.33	9.38	11.68
Mar. 5	18.0	746	1.48	2.43	4.23	6.87	9.19
Jan. 31	15.0	735	1.99	3.76	6.07	8.38	10.27
Mar. 10	15.0	743	1.48	2.42	4.01	6.12	7.81
Mar. 11	12.0	746	1.27	2.11	3.28	5.08	6.57
Mar. 12	9.0	....	.95	1.59	2.33	3.80	4.97

[a] Initial oxygen percentage maintained by admitting to apparatus pure oxygen in measured amounts.

ADDITION OF CARBON DIOXIDE TO ATMOSPHERE.

Tests to determine the effect of carbon dioxide in the atmosphere acting upon the coal were made with coal No. 48 (Illinois). The proportion of oxygen was kept constant; the temperature was kept at about 200° C. The results are given in Table 7.

TABLE 7.—*Rates of oxidation of coal in air as affected by different percentages of carbon dioxide (oxygen remaining constant).*

[Coal No. 48 (Illinois). Temperature 200° C., fineness 80 to 100 mesh.]

Date of test.	Carbon dioxide in atmosphere.	Barometer reading.	Amount of oxygen consumed per gram of dry coal in—				
			5 minutes.	10 minutes.	20 minutes.	40 minutes.	60 minutes.
1913.	*Per cent.*	*Mm.*	*C. c.*	*C. c.*	*C. c.*	*C. c.*	*C. c.*
Feb. 17	0.0	742	2.24	3.52	5.34	8.35	10.91
Feb. 18	1.0	752	2.24	3.52	5.23	....	10.91
Feb. 19	2.0	746	2.24	3.32	5.23	8.32	11.02
Feb. 20	4.0	744	2.03	3.20	5.12	8.34	10.71
Feb. 26	10.0	745	2.03	3.32	5.23	8.55	10.91

DISCUSSION OF RESULTS OF TESTS.

Table 4 and figure 4 show the large influence of temperature on the rate of oxidation. The relatively small difference in rate indicated between 170° and 240° is due, as before mentioned, to the large error caused by incomplete removal of carbon dioxide.

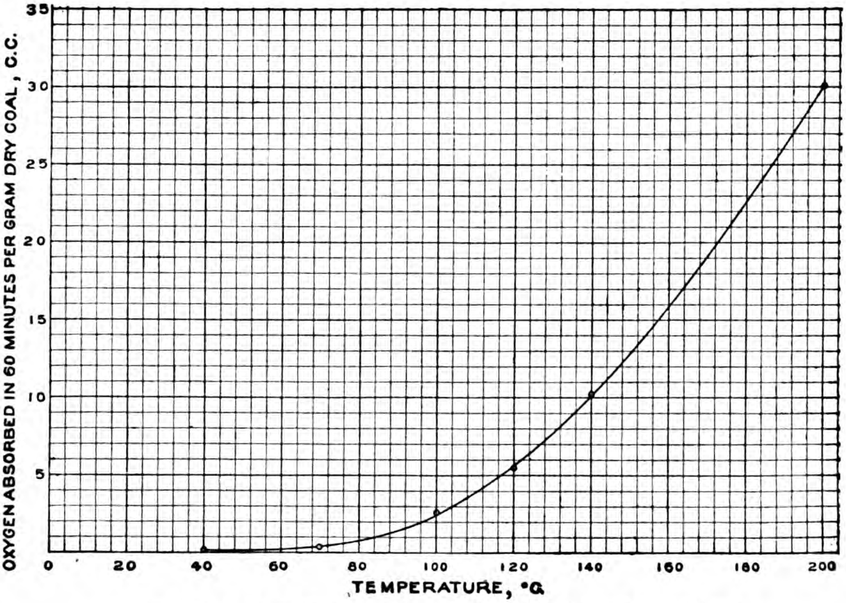

FIGURE 4.—Rate of oxidation of coal No. 48 (Illinois) at different temperatures.

Tables 5 and 6 and figures 5 and 6 are designed to show the influence of the concentration of oxygen present on the rate. In pure oxygen (Table 5) the concentration appears to have less effect on the rate than it does in air, although the influence is clearly seen in both cases. It seems that the oxygen percentage must be reduced below 15 per cent in air or to a pressure of about 100 mm. when pure oxygen is used before the effect on the rate of oxidation becomes serious. The tests made in air are subject to a considerable error, due to an obstructing effect of the nitrogen on the diffusion of O_2, N_2, CO_2, and water vapor.

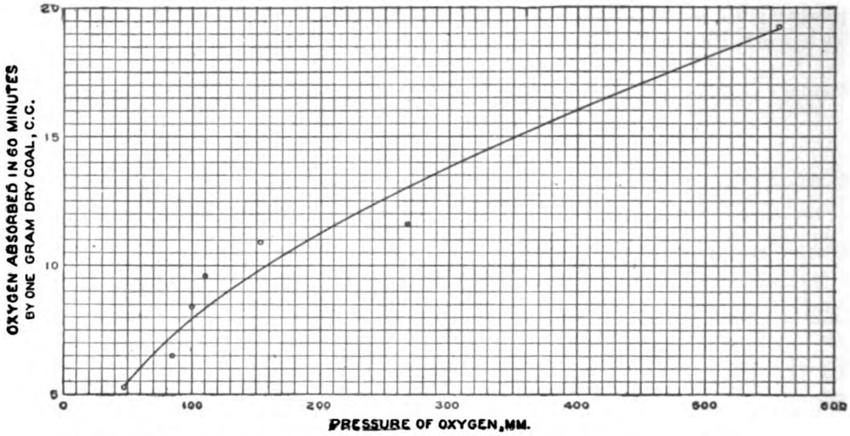

FIGURE 5.—Rate of oxidation of coal No. 48 (Illinois) under varying pressures of oxygen.

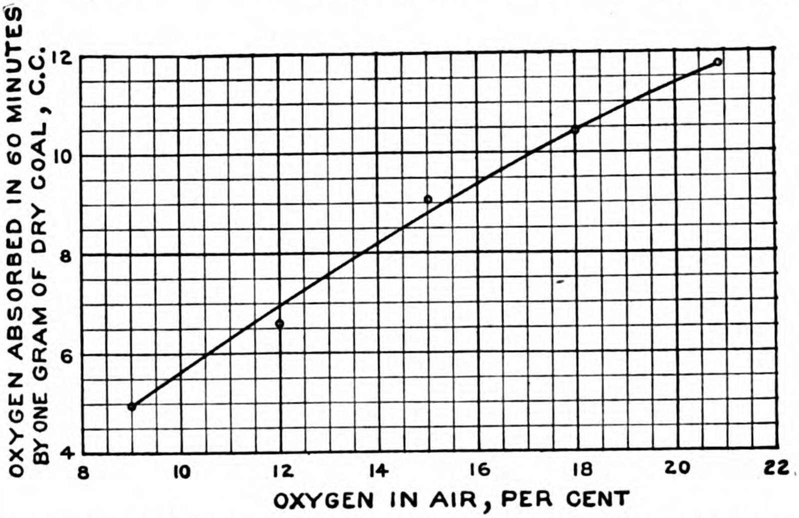

FIGURE 6.—Rate of oxidation of coal No. 48 (Illinois), as affected by percentage of oxygen in the air.

Table 7 shows that in a constant concentration of oxygen the presence of as much as 10 per cent of carbon dioxide in the atmosphere has no retarding influence on the rate of oxidation at 200° C. Whether this would also be true at higher temperatures, where the reaction tends to produce carbon dioxide much more rapidly, is uncertain.

EXPERIMENTS TO DETERMINE NATURE OF OXIDATION REACTIONS.

In order to determine the nature of the oxidation process and how it is affected by a change of conditions, an experimental method was adopted by which, primarily, the products of the reactions were measured. The rate of reaction was not determined, nor was the method reliable for comparing different coals as to the quantities of products formed in a given time. The method was designed rather to show qualitatively the nature of the products and the effect produced thereon by the temperature of heating, and to determine whether at the different temperatures there exists any definite relationship between the different products.

DESCRIPTION OF APPARATUS AND OF METHODS USED.

A 1-gram sample of dry coal, 80 to 100 mesh, was heated in a rapid current of dry air for an hour. The products were collected and weighed, and the change in weight of the coal itself was carefully determined. Figure 7 is a sketch of the apparatus used. The heating tube (*b*) consisted of a glass bulb 35 mm. long and 22 mm. in diameter, with inlet and outlet tubes at the same end for convenience in weighing. The outlet tube passed through to the opposite end of the bulb, and both tubes were provided with stopcocks. The inlet tube was of 5 mm. bore and had the stopcock on a right-angled branch, the straight arm being provided with a stoppered opening at the end for introducing the sample.

The heating tube was inclosed in a cylindrical electric heater 15 cm. long and 30 mm. in diameter, lined with sheet copper to equalize the temperature. Plugs of mineral wool were placed in the ends of the heater. Temperatures up to 350° C. were taken with a calibrated mercury thermometer graduated in one-half degrees; above that temperature, with a copper "constantan" thermocouple.

The current of air was at the rate of 8 to 10 liters per hour and was thoroughly dried by passing through two sulphuric acid wash bottles and a 6-inch U-tube of phosphorus pentoxide on glass wool. Carbon dioxide was removed from the air by passing it through a large wash bottle containing strong KOH solution on glass beads. A blank test at 140° C. with the average speed of air current showed a gain of 0.3

mg. in the moisture-collecting tube, a loss of 0.5 mg. in the CO_2 collecting bulb, and a gain of 0.4 mg. in the CO collecting bulb.

Water was collected and weighed in a glass-stoppered U-tube containing phosphorus pentoxide on glass wool; CO_2 in a Vanier potash bulb; and CO by oxidation to CO_2 by iodine pentoxide contained in a tube 50 cm. long heated to 160° to 170° C., and absorption of the resulting CO_2 in a second Vanier potash bulb. This method of CO determination was carefully tested by analysis of known mixtures, and the results showed that amounts of less than 200 mg. of CO passing in one hour were completely oxidized under the above-named conditions of temperature and length of column. It was necessary to use an unusually efficient CO_2 absorbing bulb, such as the Vanier type, in order to effect complete absorption in so rapid a current. The absence of more than traces of unsaturated hydrocarbons, which would react with I_2O_5 as does CO, was assumed at oxidation temperatures below 300° C.

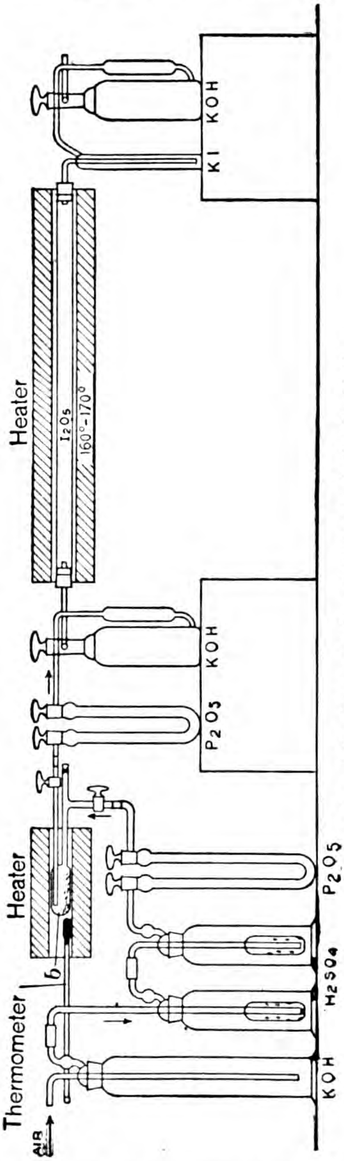

FIGURE 7.—Apparatus for measuring products of oxidation.

The coal was dried in a vacuum over sulphuric acid for a period of at least seven days, a number of 1-gram samples being weighed out at one time and dried simultaneously. The dry weight was taken in a closed weighing bottle and the coal transferred as quickly as possible to the heating tube.

At the end of an hour the tube was withdrawn from the heater and the air current continued for five minutes in order to sweep out the gaseous products from the bulb and the connecting tubes.

In order to correct the results for volatile products arising from destructive distillation of the coal, parallel tests were made in which nitrogen was used in place of air. A supply of commercial nitrogen containing about 8 per cent of oxygen was passed through two wash bottles containing alkaline pyrogallol solution and then over a heated copper-gauze roll 6 inches long to remove the last traces of oxygen, the products being collected and measured as in the experiments in which an air current was used.

RESULTS OF TESTS.

The results, computed on the basis of dry coal, are given in Tables 8 to 11.

TABLE 8.—*Water produced by oxidation of three coals—No. 43 (Wyoming), No. 48 (Illinois), and No. 650 (Pittsburgh)—at different temperatures.*

[Milligrams per gram of dry coal.]

Temperature.	Water produced in air current.			Water produced in nitrogen current.			Water due to oxidation.[a]		
	43	48	650	43	48	650	43	48	650
° C.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
110	9.8	4.0	....	....	....	....	7.8	3.6	....
140	18.2	12.3	10.6	....	1.9	1.8	14.4	10.4	8.8
140	21.2	9.6	6.6	....	....	....	17.4	7.7	4.8
170	31.1	24.6	9.6	....	5.9	....	23.3	18.7	7.3
170	34.9	24.1	7.4	....	....	....	27.1	18.2	5.1
200	60.3	48.7	19.0	11.2	....	2.7	49.1	40.4	16.3
200	63.8	51.8	18.2	....	....	....	52.6	43.5	15.5
230	104.2	89.0	45.1	....	....	....	89.2	78.3	40.0
230	93.6	92.6	....	....	....	....	78.6	81.9	....
230	96.8	....	....	....	....	....	81.8	....	....
260	156.6	138.9	84.2	18.2	13.1	7.5	138.4	125.8	76.7
260	161.8	132.2	....	....	....	....	143.6	119.1	....
290	....	161.4	108.0	....	....	....	....	147.8	97.5
320	287.0	236.0	....	34.5	14.1	....	252.5	221.9	....

[a] For certain temperatures an approximate value for the water produced in a current of nitrogen was estimated on the basis of actual results at three or more other temperatures.

TABLE 9.—*CO_2 produced by oxidation of three coals—No. 43 (Wyoming), No. 48 (Illinois), and No. 650 (Pittsburgh)—at different temperatures.*

[Milligrams per gram of dry coal.]

Temperature.	CO_2 produced in air current.			CO_2 produced in nitrogen current.			CO_2 due to oxidation.[a]		
	43	48	650	43	48	650	43	48	650
° C.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
110	1.1	0.6	....	....	....	....	0.7	0.3	0.4
140	6.8	1.9	2.8	1.4	0.4	0.5	5.4	1.5	2.3
140	4.9	1.2	....	....	....	....	3.5	.8	....
170	13.8	4.7	1.4	2.4	.6	....	11.4	4.1	.8
170	11.7	4.2	....	....	....	....	9.3	3.6	....
200	25.7	14.4	4.3	3.4	.7	....	22.3	13.7	3.7
200	34.2	17.2	6.0	....	....	....	30.8	16.5	5.4
230	78.2	47.7	17.0	4.8	.9	....	73.4	46.8	16.3
230	73.2	....	....	....	....	....	68.4	....	....
230	81.2	....	....	....	....	....	76.4	....	....
260	239.5	81.3	48.2	6.3	1.3	.8	233.2	80.0	47.4
260	192.8	81.9	....	8.3	....	....	184.5	80.6	....
290	....	141.3	80.0	....	....	....	....	137.0	79.0
320	1,019.0	395.0	....	17.2	7.2	....	1,001.8	386.8	....

[a] In some tests CO_2 produced in a current of nitrogen was estimated approximately on the basis of actual results at three or more temperatures.

TABLE 10.—*CO produced by oxidation of three coals—No. 43 (Wyoming), No. 48 (Illinois), and No. 650 (Pittsburgh)—at different temperatures.*

[Milligrams per gram of dry coal.]

Temperature.	CO produced in air current.			CO produced in nitrogen current.			CO due to oxidation.		
	43	48	650	43	48	[a] 650	43	48	[a] 650
°*C.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
110	3.8	0.5	....	....	....	....	3.8	0.5	....
140	3.4	2.0	3.0	....	....	....	3.4	2.0	....
140	2.8	.8	2.8	....	....	....	2.8	.8	....
170	4.1	1.8	2.5	....	....	....	4.0	1.8	....
170	2.9	1.9	....	....	....	....	2.8	1.9	....
200	10.2	7.0	4.1	0.2	....	....	10.0	7.0	....
200	10.3	....	4.2	....	....	....	10.1	....	....
230	20.7	11.6	7.8	.7	....	....	20.0	11.2	....
230	18.0	13.3	....	....	....	....	17.3	12.9	....
230	21.1	....	....	....	....	....	20.4	....	....
260	43.3	23.8	16.2	1.7	1.4	....	41.6	22.4	....
260	39.1	25.4	....	....	....	....	37.4	24.0	....
290	....	39.2	27.4	....	....	....	....	36.7	....
320	167.3	108.6	....	4.1	3.4	....	163.2	105.2	....

[a] In the tests with coal 650 determinations of CO produced in a current of nitrogen were not made, but on the basis of the small amount of CO_2 produced the amount may be assumed to be almost negligible.

TABLE 11.—*Change in weight of three coals—No. 43 (Wyoming), No. 48 (Illinois), and No. 650 (Pittsburgh)—caused by oxidation at different temperatures.*

[Milligrams per gram of dry coal.]

Temperature.	Total loss or gain in weight in air current.			Loss due to carbon and hydrogen burned (calculated from CO_2, CO, and H_2O formed) plus loss due to distillation.			Net change in weight due to oxygen fixation.[a]		
	43	48	650	43	48	650	43	48	650
° *C.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
110.....	− 6.7	+ 1.1	....	5.0	1.4	....	− 1.7	+ 2.5	....
140.....	− 10.0	+ 3.9	− .7	9.2	4.8	5.3	− .8	+ 8.7	+ 4.6
140.....	− 11.3	+ 1.3	− .8	9.6	3.7	4.1	− 1.7	+ 5.0	+ 3.3
170.....	− 14.4	+ 10.3	+ 2.9	17.5	10.3	4.8	+ 3.1	+20.6	+ 7.7
170.....	− 16.1	+ 12.1	+ 3.6	17.1	10.2	3.8	+ 1.0	+22.3	+ 7.4
200.....	− 25.4	+ 22.1	+14.4	30.5	17.5	8.3	+ 5.1	+39.6	+22.7
200.....	− 27.6	+ 22.2	+10.0	33.2	20.1	7.8	+ 5.6	+42.3	+17.8
230.....	− 44.0	+ 24.8	+22.1	58.8	34.9	17.9	+14.8	+59.7	+40.0
230.....	− 30.5	+ 26.1	....	55.2	39.7	....	+24.7	+65.8	....
230.....	− 42.2	....	....	59.0	....	....	+16.8	....	....
260.....	−104.6	+ 10.9	+23.8	123.4	62.7	36.4	+18.8	+73.6	+60.2
260.....	− 95.7	+ 11.4	....	109.4	61.0	....	+13.7	+72.4	....
290.....	....	− 15.3	+ 7.8	....	90.5	55.6	....	+75.2	+63.4
320.....	−524.0	−154.0	....	427.2	211.0	....	−96.8	+57.0	....

[a] No loss of volatile products other than H_2O, CO_2, and CO being assumed. Below 300° C. the tests in nitrogen showed good agreement between loss in weight and total products collected.

CONCLUSIONS FROM RESULTS OF TESTS.

The experimental results given in Tables 8 to 11 do not show good agreement between check determinations. Coal is neither a pure nor a uniform substance, and it was not practicable in these tests to keep the experimental conditions absolutely constant. Many errors may have arisen from variations in the temperature, in the rapidity of the air current, previous exposure of the coal, oxidation during transfer of the coal, density or structure of the coal, and the position of the sample in the heating tube. Although deviations of 10 per cent from the mean are therefore not surprising, the general trend of the results is evident, in spite of such a large apparent percentage error in individual determinations.

The curves in figures 8 to 10 show the amounts of H_2O, CO_2, and CO formed by the oxidation of the different coals [No. 43 (Wyoming), No. 48 (Illinois), and No. 650 (Pittsburgh)] at temperatures ranging from 110° to 320° C.

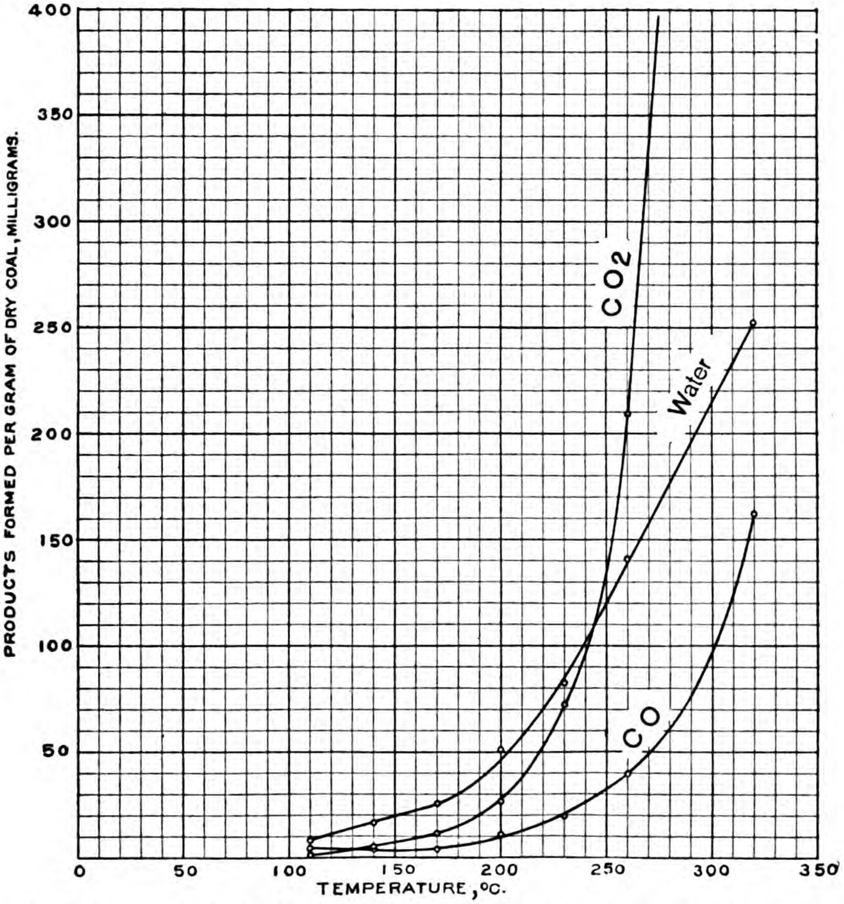

FIGURE 8.—Amounts of water, CO_2, and CO produced in the oxidation of coal No. 43 (Wyoming).

It is evident that the first step in the oxidation of coal is the formation of an addition compound, or complex, of oxygen with one or more of the substances present in coal. This complex is unstable and decomposes readily—more readily in the case of some coals than of others—setting free water, CO_2, and CO. More water than CO_2 is formed by the oxidation at temperatures below 200° C. and, with some kinds of coal, even up to 300°. A considerable proportion of carbon monoxide is found in the products of oxidation, even though a large excess of air is present. In view of the very low velocities, at the temperatures used, of the reactions by which CO is produced from carbon by the action of CO_2 or H_2O, it is likely that the CO found is the direct result of decomposition of the oxygen complex of the coal substance. It may be seen from Table 11 that the oxygen complex of the Wyoming coal decomposes much more easily than do those of the Illinois and Pittsburgh coals. In tests made with the Wyoming coal larger amounts of products are obtained and practically no oxygen fixed between 100° and 200° C. under the influence of the rapid current of dry air; the Illinois and Pittsburgh coals, on the other hand, show increases in weight up to 260° in spite of the loss of carbon and hydrogen in CO_2, CO, and H_2O.

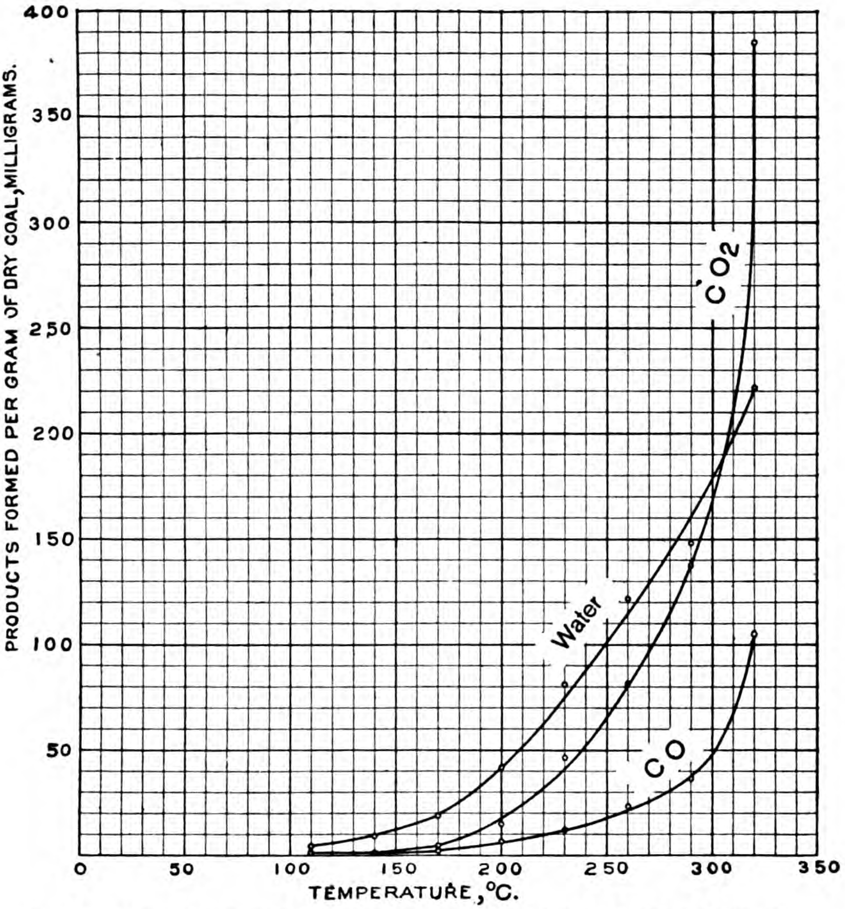

FIGURE 9.—Amounts of water, CO_2, and CO produced in the oxidation of coal No. 48 (Illinois).

RELATIVE QUANTITIES OF PRODUCTS OF OXIDATION.

It is of interest to determine whether for different temperatures and different coals any definite relationship exists between one product and any other, or among the three products expressed as percentages of their total; whether at the lower temperatures water is the predominating product from all coals, and at what temperature for each coal the oxides of carbon begin to predominate in the products. By plotting curves representing these products as percentages in a ternary diagram (fig. 11), in which the point representing 100 per cent of any one of the three constituents is placed at one apex of an equilateral triangle and lower percentages fall on the perpendiculars to the opposite side of the triangle, any regularity of relationship between the three constituents becomes at once evident. We see (fig. 11) that for the same coal the oxidation product is of a different composition at different temperatures, and different coals yield products of different composition at the same temperature. It is to be noted, however, that for a given coal the products of oxidation at different temperatures are so related to each other that when plotted on the diagram the points representing the proportions in which they occur fall nearly upon a straight line within a certain range of temperature. In other words, the composition of the products is determined by a definite law that may be expressed by an equation. The percentage composition is not constant, but for any given percentage of one constituent the percentage of either of the others is fixed according to a definite relationship that varies with different coals. In general, however, as the temperature rises, the ratio of CO_2+CO to H_2O increases, and there is a more or less constant

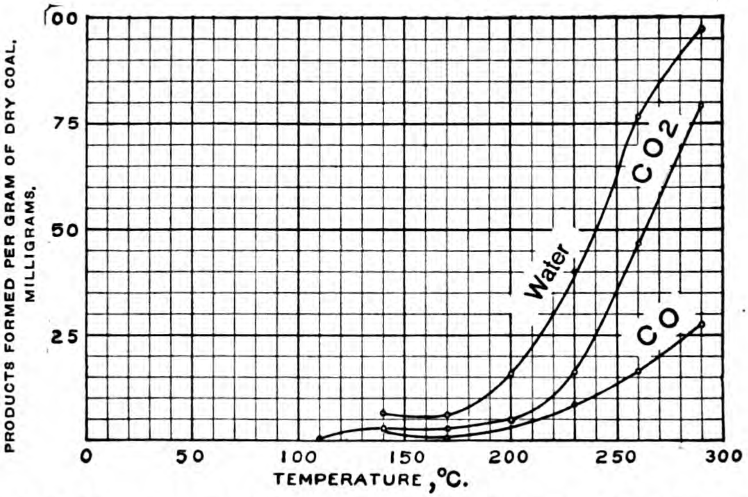

Figure 10.—Amounts of water, CO_2, and CO produced in the oxidation of coal No. 650 (Pittsburgh).

relationship between CO_2 and CO, as shown by the tendency of the line indicating compositions to approach an apex of the triangle.

NATURE OF THE OXIDIZING ACTION.

There is no indication, therefore, that a uniform complex is produced from different coals by oxidation, but it is probable that in each coal several different complexes are formed, the same ones occurring possibly in all coals, but in different proportions. In one coal the complex may break up more rapidly than in another and may produce a larger proportion of water or of CO_2. In general, however, oxidation at temperatures below 200° C. tends both to fix oxygen and to form products in which water predominates, whereas above that temperature there is little or no fixation of oxygen, and CO_2 begins to predominate in the products. An easily ignited coal begins to produce CO_2 in large proportion at lower temperatures than a coal that is more difficult to ignite. Curves plotted in figure 12 show the net increase in weight in coals No. 43 (Wyoming), No. 48 (Illinois), and No. 650 (Pittsburgh) by fixation of oxygen.

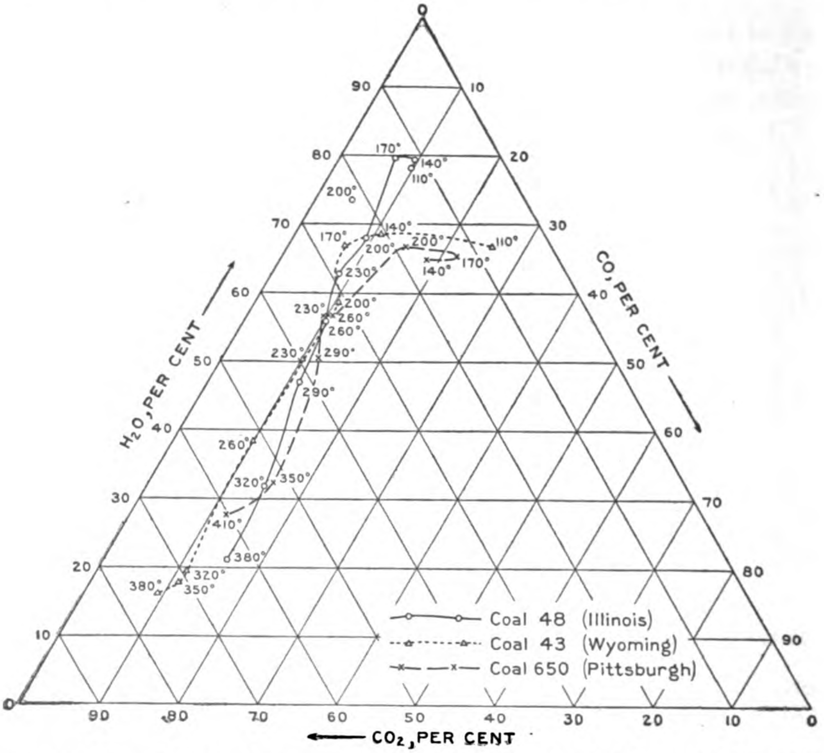

FIGURE 11.—Composition of oxidation products from coals No. 43 (Wyoming), No. 48 (Illinois), and No. 650 (Pittsburgh).

Inasmuch as there are probably only traces of free carbon and probably no free hydrogen in coal, there seems to be, when coal burns, no possibility of the direct formation of CO_2, CO, or H_2O from the elements, unless it may be assumed that a preliminary distillation of volatile matter, that leaves a residue of free carbon in the form of coke, takes place. Such an assumption is hardly justified, in view of the facts that coal does not completely set free its volatile matter below 900° to 1,000° C., that considerable time is ordinarily required to heat the coal to that temperature, and that during this time under the usual conditions of furnace combustion the coal is surrounded by oxygen and is undergoing oxidation in the manner described above.

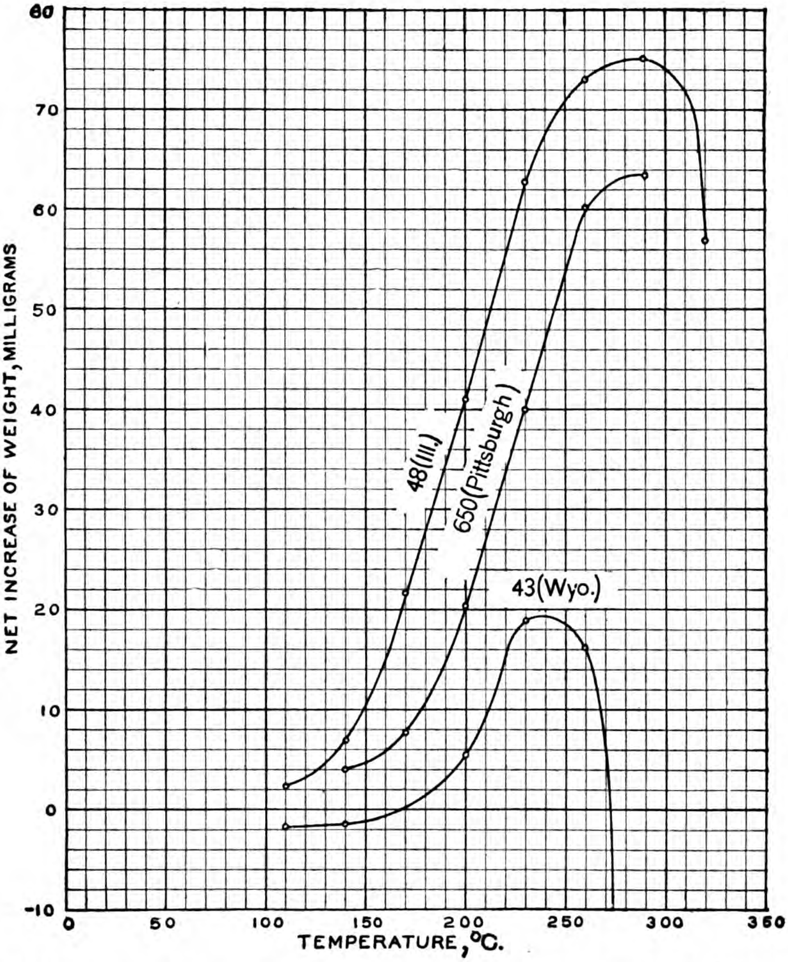

FIGURE 12.—Increase of weight in coals No. 43 (Wyoming), No. 48 (Illinois), and No. 650 (Pittsburgh), by oxygen fixation.

The combustion of some hydrocarbons has been shown by Bone[a] to involve an intermediate formation of an oxygenated molecule which decomposes into the final products CO_2 and H_2O. Rhead and Wheeler[b] at the coal-dust experiment station of the British Home Office, who have studied the mode of combustion of carbon, advance the hypothesis, which is supported by experimental evidence, that "in the normal burning of carbon the carbon dioxide and carbon monoxide found as the apparently primary products of combustion arise from the decomposition at the temperature of combustion of a complex, the formation of which is the first result of the encounters between oxygen and carbon molecules." Their work was done with charcoal. They consider the complex formed to be physical-chemical, no definite molecular formula being assigned to it, and a high temperature or reduced pressure being required for its decomposition.

INFLAMMABILITY OF COAL DUST.

Investigators in England[c] and in France[d] have advanced the theory that, assuming like conditions as to fineness of division, percentage of inert material, and amount of previous exposure, the variation in degree of inflammability of different coal dusts suspended in air is due largely to ease of decomposition by heat, or, in other words, to the relative amount and character of the volatile products distilled from the coal by moderate heating.

The following considerations call attention to another factor that probably influences the inflammability of coal more than does the amount or character of the volatile matter itself. Comparative inflammability tests at the Bureau of Mines laboratories[e] of the four kinds of coal used in the investigation of oxidation herein described (pp. 9–12) have shown that coal No. 43[f] (Wyoming), in spite of its large water content is much more highly inflammable than any of the others, and that the three other coals follow it in order of decreasing inflammability, as follows:

No. 48 (Illinois)[g], No. 395 or 650 (Pittsburgh)[h], and No. 9614 (W. Va.)[i].

---

[a] Bone, W. A., and others, The slow oxidation of methane at low temperatures: Jour. Chem. Soc. (London), vol. 81, pt. 1, 1902, p. 536, vol. 83, pt. 2, 1903, p. 1074; The slow combustion of ethane, vol. 85, pt. 1, 1904, p. 693; The combustion of ethylene, vol. 85, pt. 2, 1904, p. 1637; The combustion of acetylene, vol. 87, pt. 2, 1905, p. 1232; The explosive combustion of hydrocarbons, vol. 89, pt. 1, 1906, p. 660.

[b] Rhead T. F. E., and Wheeler, R. V., The mode of combustion of carbon. Jour. Chem. Soc. (London), vol. 103, 1913, pp. 461, 1210.

[c] Second Report, Explosions in Mines Committee, British Home Office, 1912.

[d] Report of First Series Laboratory Investigations, French Collieries Commission, May, 1912.

[e] Frazer, J. C. W., Hoffman, E. J., and Scholl, L. A., jr., A laboratory study of the inflammability of coal dust: Bull. 50, Bureau of Mines, 1913.

[f] Same kind of coal as No. 12008 in Bull. 50, Bureau of Mines, p. 42.

[g] Same kind of coal as No. 10959 in Bull. 50, Bureau of Mines, p. 23.

[h] Same kind of coal as No. 11163 in Bull. 50, Bureau of Mines, p. 20.

[i] Same kind of coal as No. 10623 in Bull. 50, Bureau of Mines, p. 16.

Digitized by Google Original from PRINCETON UNIVERSITY

Studies[a] of the volatile matter produced from these same coals have shown that the volatile gases from coal No. 43 (Wyoming) and from No. 48 (Illinois) (the more inflammable of the four coals) contain relatively large proportions of water of decomposition and CO_2, which probably tend to retard the ignition of inflammable gases. No experimental evidence has been obtained to show that the volatile matter produced by the usual methods of coal-dust ignition is distilled from coal during the momentary period of heating prevailing in the ignition of coal dust, or that, if any such is distilled, the amount is sufficient to become a factor in ignition. Even if such preliminary distillation occurs, it does not seem likely, in view of the nature of the early volatile matter from the more inflammable coals, that the inflammability of the coal is determined thereby.

Relative rapidity of oxidation can, on the other hand, reasonably be regarded as an index to the degree of inflammability of a combustible material, since ignition is so largely a process of oxidation. Oxidation is an exothermic process, producing heat even in its initial stages, and the rate of oxidation rapidly increases with rise of temperature; therefore oxidation is self-promoting and may increase its own intensity with explosive rapidity under favorable conditions. Distillation of coal, on the other hand, is, in its early stages, endothermic, and is therefore not self-promoting, but tends to withdraw heat from surrounding sources.

Although frequent irregularities occur, the relative inflammability of coal dusts suspended in air is found to vary approximately as the percentage of volatile matter in the coal. This fact does not, however, establish any causative influence of one variable on the other.

In the coals thus far tested the comparative rate of oxidizability also varies approximately as the percentage of volatile matter; therefore the rate of oxidizability may perhaps be a truer index of inflammability than the percentage of volatile matter.

A simple test for comparative oxidizability of combustible materials is desirable, for oxidizability may prove to be an index of the relative "ignition points" of the materials or their degrees of inflammability when suspended as dusts.

OTHER CONCLUSIONS FROM RESULTS OF TESTS.

The comparative tendency of different coals to deteriorate in storage or to develop heat spontaneously conforms to their relative oxidizability.

The effect of weathering or of preliminary moderate heating on the coking quality of coal is explained as an effect of oxidation whereby the fusible organic constituents of the coal are decomposed or altered. The alteration does not occur in a nonoxidizing atmosphere.

---

[a] Porter, H. C., and Ovitz, F. K., The volatile matter of coal: Bull. 1, Bureau of Mines, 1910, 56 pp.

It is known that weathering of coal causes an increase of "combined" water; that is, of water that is not in the normal free state and that has at any given temperature a vapor pressure lower than the normal. This water remains in the coal after "air-drying." Its increase by weathering is due to oxidation and to the formation thereby of a complex easily decomposed by heat so as to yield water.

The official methods of analysis for coal, recommended by a committee of the American Chemical Society, prescribe a preliminary air-drying procedure to bring the sample into moisture equilibrium with the air and to minimize alteration during exposure. For certain kinds of high moisture coals this air-drying process requires from two to four days at 30° to 35° C. It will be seen from the experiments to determine the oxidation of coal previously described that an error is thus introduced into the analysis through the formation of an oxygenated complex that decomposes on drying at 105° C. and yields an amount of water in excess of the true original content of the coal. The official method for determining moisture prescribes drying in air at 105°. With some coals errors due to oxidation also enter into this process through an increase of weight from oxygen absorption, and, when water is determined by direct weighing, from the production of an excessive amount of water through the breaking down of the oxygenated complex.

In a sealed area of a coal mine or in a place where there is no ventilation, the oxygen content of the air is rapidly reduced by absorption in the coal. If the coal becomes warmed in gob piles or elsewhere by spontaneous heating, appreciable quantities of carbon monoxide may be formed by oxidation. When a fire area in a mine has been sealed in order to extinguish the fire by reducing the air supply, the analyses of gas samples from behind stoppings give indications of the progress of the fire. As in the oxidation of coal considerable carbon monoxide is formed at temperatures as low as 200° to 300° C., its presence in mine-fire gases may not always indicate active combustion, but it does indicate a temperature high enough to reignite the coal when an adequate air supply is admitted.

PUBLICATIONS ON FUEL TECHNOLOGY.

Limited editions of the following Bureau of Mines publications are temporarily available for free distribution. Requests for all publications can not be granted and applicants should select only those publications that are of especial interest to them. All requests for publications should be addressed to the Director, Bureau of Mines, Washington, D. C.:

BULLETIN 1. The volatile matter of coal, by H. C. Porter and F. K. Ovitz. 1910. 56 pp., 1 pl., 9 figs.

BULLETIN 2. North Dakota lignite as a fuel for power-plant boilers, by D. T. Randall and Henry Kreisinger. 1910. 42 pp., 1 pl., 7 figs.

BULLETIN 3. The coke industry of the United States as related to the foundry, by Richard Moldenke. 1910. 32 pp.

BULLETIN 4. Features of producer-gas power-plant development in Europe, by R. H. Fernald. 1910. 27 pp., 4 pls., 7 figs.

BULLETIN 6. Coals available for the manufacture of illuminating gas, by A. H. White and Perry Barker, compiled and revised by H. M. Wilson. 1911. 77 pp., 4 pls., 12 figs.

BULLETIN 7. Essential factors in the formation of producer gas, by J. K. Clement, L. H. Adams, and C. N. Haskins. 1911. 58 pp., 1 pl., 16 figs.

BULLETIN 12. Apparatus and methods for the sampling and analysis of furnace gases, by J. C. W. Frazer and E. J. Hoffman. 1911. 22 pp., 6 figs.

BULLETIN 13. Résumé of producer-gas investigations, October 1, 1904, to June 30, 1910, by R. H. Fernald and C. D. Smith. 1911. 393 pp., 12 pls., 250 figs.

BULLETIN 14. Briquetting tests of lignite at Pittsburgh, Pa., 1908–9; with a chapter on sulphite-pitch binder, by C. L. Wright. 1911. 64 pp., 11 pls., 4 figs.

BULLETIN 16. The uses of peat for fuel and other purposes, by C. A. Davis. 1911. 214 pp., 1 pl., 1 fig.

BULLETIN 18. The transmission of heat into steam boilers, by Henry Kreisinger and W. T. Ray. 1912. 180 pp., 78 figs.

BULLETIN 23. Steaming tests of coals and related investigations, September 1, 1904, to December 31, 1908, by L. P. Breckenridge, Henry Kreisinger, and W. T. Ray. 1912. 380 pp., 2 pls., 94 figs.

BULLETIN 24. Binders for coal briquets, by J. E. Mills, 56 pp., 1 fig. Reprint of United States Geological Survey Bulletin 343.

BULLETIN 27. Tests of coal and briquets as fuel for house-heating boilers, by D. T. Randall. 44 pp., 3 pls., 2 figs. Reprint of United States Geological Survey Bulletin 366.

BULLETIN 29. The effect of oxygen in coal, by David White. 80 pp., 3 pls. Reprint of United States Geological Survey Bulletin 382.

BULLETIN 30. Briquetting tests at the United States fuel-testing plant at Norfolk, Va., 1907–8, by C. L. Wright. 41 pp., 9 pls. Reprint of United States Geological Survey Bulletin 385.

BULLETIN 32. Commercial deductions from comparisons of gasoline and alcohol tests in internal-combustion engines, by R. M. Strong. 38 pp. Reprint of United States Geological Survey Bulletin 392.

BULLETIN 36. Alaskan coal problems, by W. L. Fisher. 1911. 32 pp., 1 pl.

BULLETIN 39. The smoke problem at boiler plants, a preliminary report, by D. T. Randall, 31 pp. Reprint of United States Geological Survey Bulletin 334, revised by S. B. Flagg.

BULLETIN 40. The smokeless combustion of coal in boiler furnaces, with a chapter on central heating plants, by D. T. Randall and H. W. Weeks. 188 pp., 40 figs. Reprint of United States Geological Survey Bulletin 373, revised by Henry Kreisinger.

BULLETIN 43. Comparative fuel values of gasoline and denatured alcohol in internal-combustion engines, by R. M. Strong and Lauson Stone. 1912. 243 pp., 3 pls., 32 figs.

BULLETIN 49. City smoke ordinances and smoke abatement, by S. B. Flagg. 1912. 55 pp.

BULLETIN 54. Foundry-cupola gases and temperatures, by A. W. Belden. 1913. 29 pp., 3 pls., 16 figs.

BULLETIN 58. Fuel-briquetting investigations, July, 1904, to July, 1912, by C. L. Wright. 1913. 277 pp., 21 pls., 3 figs.

BULLETIN 63. Sampling coal deliveries, and types of Government specifications for the purchase of coal, by G. S. Pape. 1913. 68 pp., 4 pls., 3 figs.

TECHNICAL PAPER 2. The excape of gas from coal, by H. C. Porter and F. K. Ovitz. 1911. 14 pp., 1 fig.

TECHNICAL PAPER 5. The constituents of coal soluble in phenol, by J. C. W. Frazer and E. J. Hoffman. 1912. 20 pp., 1 pl.

TECHNICAL PAPER 8. Methods of analyzing coal and coke, by F. M. Stanton and A. C. Fieldner. 1913. 42 pp., 12 figs.

TECHNICAL PAPER 16. Deterioration and spontaneous combustion of coal in storage, a preliminary report, by H. C. Porter and F. K. Ovitz. 1912. 14 pp.

TECHNICAL PAPER 20. The slagging type of gas producer, with a brief report of preliminary tests, by C. D. Smith. 1912. 14 pp., 1 pl.

TECHNICAL PAPER 31. Apparatus for the exact analysis of flue gas, by G. A. Burrell and F. M. Seibert. 1913. 12 pp., 1 fig.

TECHNICAL PAPER 55. The production and use of brown coal in the vicinity of Cologne, Germany, by C. A. Davis. 1913. 15 pp.